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14. ABSTRACT

Funding for this project was used to purchase three research grade instruments: a mini twin-screw extruder, a dynamic mechanical analyzer, and a benchtop powder x-ray diffractometer. The new equipment has been used to prepare materials for fire testing, to assess crystallinity of our composite materials, and to examine the effects of flame retardants on the viscoelastic properties of the composites. Results have indicated that the use of POSS-modified cellulose improves multiple properties of poly(lactic acid) and has significant advantages over conventional intumescing flame retardant additives. Furthermore, the equipment has been used to assess the properties of similar materials prepared in other collaborative projects. The measurements have already resulted in one publication, and several other manuscripts are in preparation. Acknowledgement to the Air Force Office of Scientific Research, including the award number for this grant, has been included in these manuscripts.

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FROM: Douglas Fox, Asst. Prof. of Chemistry, American University

RE: Final Report on "POSS-Modified Cellulose for Improved Biopolymer Performance" (AFOSR-DURIP Grant #FA9550-10-1-0323)

DATE: September 30, 2011

Summary

Funding for this project was used to purchase three research grade instruments: a mini twin-screw extruder, a dynamic mechanical analyzer, and a benchtop powder x-ray diffractometer. The new equipment has been used to prepare materials for fire testing, to assess crystallinity of our composite materials, and to examine the effects of flame retardants on the viscoelastic properties of the composites. Results have indicated that the use of POSS-modified cellulose improves multiple properties of poly(lactic acid) and has significant advantages over conventional intumescing flame retardant additives. Furthermore, the equipment has been used to assess the properties of similar materials prepared in other collaborative projects. The measurements have already resulted in one publication, and several other manuscripts are in preparation. Acknowledgement to the Air Force Office of Scientific Research, including the award number for this grant, has been included in these manuscripts.

Relevance to AFOSR

Polymers and composites are becoming the material of choice for a number of applications related to the U. S. Air Force. Although there are specialty needs for high performance polymers, such as polycarbonate or epoxies, commodity plastics, such as polystyrene or low grade polyesters, are in demand for everyday materials. Specific to the Air Force, these materials have been used in concrete, electronic systems, packaging materials, and upholstery. Poly(lactic acid) is a suitable biodegradable and renewable replacement for low grade polyesters, which can reduce our energy needs and dependence on petroleum. Furthermore, poly(lactic acid) has shown promise in biomedical applications, such as medical implants, surgical sutures, and tissue scaffolding. To improve the low impact strength, poor elongation properties, and slow crystallization exhibited by this polymer, we proposed to synthesize and characterize poly(lactic acid) nanocompoistes using POSS-modified cellulose nanofibrils as a reinforcing filler.

Acquired Research Equipment

The funds from this grant were used to purchase a mini twin-screw extruder, a dynamic mechanical analyzer, and a powder x-ray diffractometer. We chose the Xplore 15 mL Compounder, manufactured by DSM Instruments because it had a larger capacity than other instruments, a quick cool mechanism for faster processing, a nitrogen stream capability to reduce humid air induced degradation of the poly(lactic acid), and a counter rotating option for better shear through the intermeshing zone of the extruder. We purchased a TA Instruments, Q-800

DMA for analyzing the viscoelastic properties of the solid nanocomposites. This instrument is easy to operate, included a liquid nitrogen cooling accessory, and uses the same software as our Differential Scanning Calorimeter to make it easier to teach to our undergraduate and MS students who will use these instruments. Finally, we purchased a Rigaku Miniflex II benchtop powder x-ray diffractometer with a monochrometer detector and 6-slot sample autochanger. This is only one of two benchtop diffractometers available, and the only one with an autochanger, which we felt was critical to make the most use of the instrument. In order to analyze all of our samples, we also needed to purchase cryogenic safety equipment for working with the liquid nitrogen, and additional sample clamp for the dynamic mechanical analyzer, additional sample holders for the x-ray diffractometer, and both a low flow pressurized gas regulator and a torque wrench for the extruder. The purchase price for these three instruments and additional accessories are provided in Table I.

Table I. Purchase price of equipment obtained through this grant

Equipment Item	Vendor	Purchase Price
Xplore 15mL mini-compounder	DSM Instruments	$141,760.00
Q-800 Dynamic Mechanical Analyzer	TA Instruments	73,300.00
Miniflex II Powder X-ray Diffractometer	Rigaku	82,144.00
Accessories	Various	2,796.00
TOTAL		$300,000.00

Project Accomplishments

A. Preliminary Results

All three instruments were purchased, installed, and calibrated within the first 6 months of the project. Much of the remaining time was devoted to preparing the nanocomposites for analysis using the extruder acquired through this grant. In particular, the heat release data using cone calorimetry requires significant amount of sample (minimum of 60 g), requiring multiple extrusions of each nanocomposite. The time and effort spent on preparing these samples was well worth it. As shown in Figure 1, our POSS-modified cellulose composites produced the best heat release rates of all composites. Furthermore, these tests revealed that the incorporation of POSS resulted in reduced smoke production during combustion.

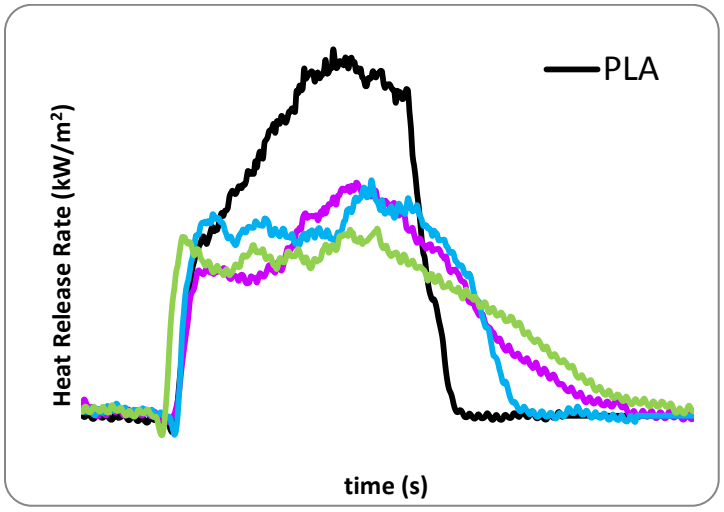

Figure 1. Heat release rate as measured by cone calorimetry of poly(lactic acid) – intumescing flame retardant composites.

During extrusion, we noted that the POSS modification exhibited additional benefits of higher melt viscosities and reduced hydrolysis of the cellulose during processing. Use of the dynamic mechanical analyzer revealed that the use of the conventional intumescent formulation of ammonium polyphosphate (APP) – pentaerythritol (PER) resulted in a significant decrease in composite stiffness and glass transition temperature (cf Figure 2). Furthermore, replacing the pentaerythritol with cellulose fibers not only prevented these losses, but also added additional stiffness to the composite. The differences observed between unmodified nanofibrillated cellulose fibers (NFC) and POSS-modified nanofibrillated cellulose fibers (PNFC) are within the margin of experimental error. This illustrates the benefit to replacing pentaerythritol with cellulosic materials, and poor stiffness and low glass transitions are two major disadvantages to poly(lactic acid).

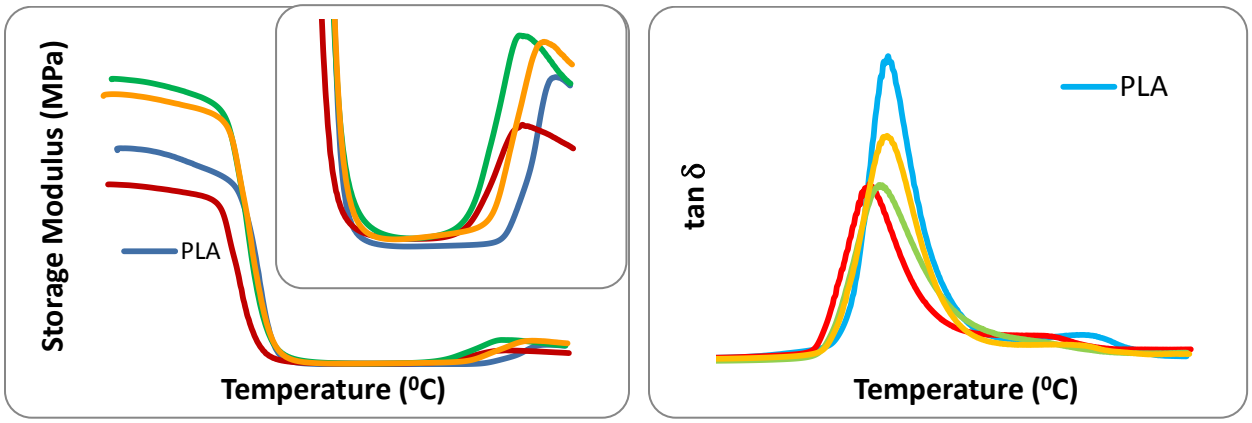

Figure 2. Dynamic mechanical analysis of poly(lactic acid) – intumescing flame retardant composites. Plots show (a) storage loss (stiffness) and (b) tan δ (T_g). The inset in (a) reduces the plot ranges to illustrate the in-situ crystallization more clearly.

The large decrease in composite stiffness and subsequent partial recovery shown in Figure 2a is indicative of amorphous material that crystallizes during the heated measurements. The inset figure shows that the crystallization begins at an earlier temperature with the addition of APP-

PER or APP-NFC, indicating a nucleating effect for the filler. The crystallization temperature is restored when using APP-PNFC, suggesting that the POSS modification reduces this nucleating effect. A similar behavior is observed for the glass transition temperature, shown in Figure 2b. This indicates that the POSS-modification reduces the changes in segmental motion when incorporating intumescing flame retardant fillers.

The fillers also had an impact on the percent crystallinity of the PLA. PLA is a semi-crystalline polymer that is known to exhibit slow crystallization kinetics. As shown in Figure 3(a), when PLA is quenched from the melt state, the polymer remains amorphous. Curing the polymer at 100 °C for 30 min results in crystallization with distinctive XRD peaks at 16.4° and 18.8°. Upon the addition of APP based intumescing flame retardants, the crystallinity of PLA is increased (cf Figure 3b). Replacing PER with NFC results in a slight decrease in crystallinity, which is restored when switching to PNFC. Comparison with differential scanning calorimetry is currently under investigation.

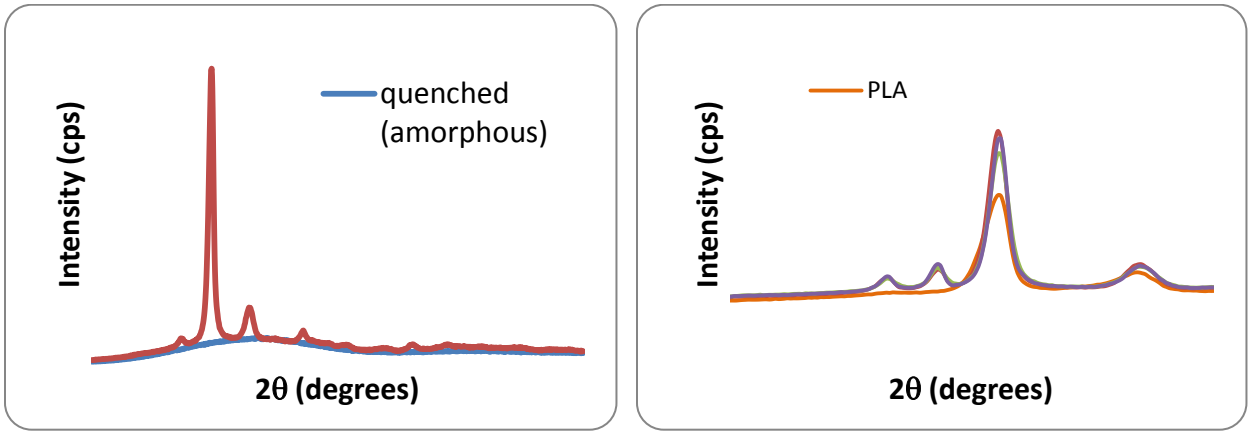

Figure 3. (a) Changes in crystallinity of pure poly(lactic acid) after curing at 100 °C for 30 min. (b) Crystallinity changes during to intumescent flame retardant fillers.

B. Future Plans

Although we have already demonstrated the effectiveness of our strategy for improving the properties of poly(lactic acid), we still have a number of unanswered questions we wish to address. The crystallinity affects the stiffness of the composite, so we still need to examine the dynamic mechanical properties of the cured samples. This can also supplement our differential scanning calorimetry results on the extent of crystallization for these composites. We also plan obtain a more complete picture of the fire properties, by conducting limiting oxygen limit and horizontal burn measurements on these composites. Finally, we continue to examine methods of attaching an acid source directly onto the cellulose fibers to eliminate the need for APP in the intumescing flame retardant formulations.

Benefits to Other Related Projects

In addition to our primary project of using POSS-modified cellulose as a reinforcing and sustainable flame retardant for poly(lactic acid), we also have used these instruments to

supplement other related projects. These collaborative projects relate to POSS, PLA, or cellulose.

A. POSS-Imidazolium Exchanged Montmorillonite

We recently submitted the manuscript, "The pillaring effect of the 1,2-dimethyl-3-(benzyl ethyl iso-butyl POSS) cation in polymer/montmorillonite nanocomposites" for publication in the journal, *Polymer*. One of the reviewers requested additional data on the thermal effects of the surfactant within the clay layer spacing. To supplement our thermal data, we included the changes in clay layer spacing and surfactant crystalline properties as indicated by powder x-ray diffraction studies. These measurements (shown in Figure 4 below) were conducted using the Miniflex II system acquired through this grant. An acknowledgement to "AFOSR under ... Award No. FA9550-10-1-0323" was included in the corrected manuscript. The manuscript has been accepted and will be published soon.

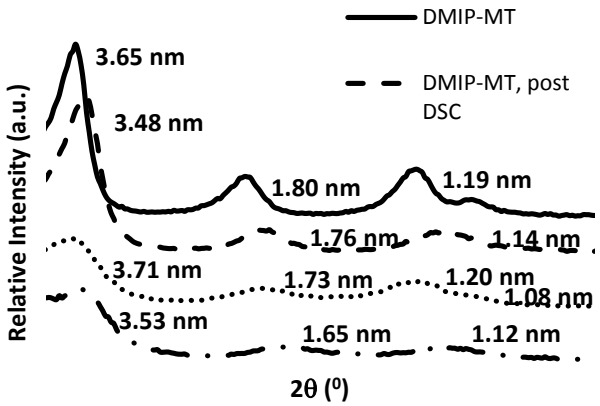

Figure 4. XRD of POSS-imidazolium exchanged clay before and 2 days after heating and cooling.

B. Cellulose Fiber Welding

One of collaborators is investigating the use of room temperature ionic liquids to fiber weld cellulose cloth samples. Ionic liquids are now well known as solvents for dissolving and processing cellulose. Cellulose cloth has a crystalline, cellulose I structure, and cellulose regenerated from ionic liquids has a more amorphous, cellulose II structure. The x-ray diffractometer is being used to quantify the amount of cellulose conversion during the welding process. A systematic study on the effects of processing conditions and coagulating bath composition on the percent conversion from cellulose I to cellulose II is currently in progress. In addition, dynamic mechanical analysis of the cloth samples is being performed to quantify the increase in stiffness that accompanies the fiber welding process.

C. Layered-Double-Hydroxide Catalyzed Poly(lactic acid)

Another collaborator is investigating the use of layered double hydroxides (LDHs) as a catalyst to synthesize clay – poly(lactic acid) composites in-situ from L,D-lactide. The phase behavior and crystallinity are being examined using differential scanning calorimetry. The x-ray

diffractometer is being used to determine crystal types, presence of starting materials, and form of the LDHs blended with the polymer matrix.